**Ab initio** Study of Small Coinage Metal Telluride Clusters $\text{Au}_n\text{Te}_m$

$(n, m = 1, 2)$

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The geometries of the most stable isomers of gold telluride systems $\text{AuTe}$, $\text{Au}_2\text{Te}$, and $\text{AuTe}_2$ are determined using the MP2 method. The aspect of gold—telluride interaction, the electron correlation, and relativistic effects on geometry and stability are investigated at the MP2 and CCSD(T) theoretical levels. The results show that the electron correlation and relativistic effects are responsible not only for gold—gold attraction but also for additional gold—telluride interaction. The gold—telluride interaction is strong enough to modify the known pattern of bare gold clusters. Both effects are essential for determining the geometry and relative stability of this type of systems.

**Keywords:** gold—telluride clusters, Møller—Plesset perturbation theory method, coupled cluster formalism

**INTRODUCTION**

The study of coinage metal mixed clusters, especially the clusters of coinage metals with group 16 atoms, is nowadays an important field of research in cluster science since the clusters present an important part of proteins and are widely used in catalysis, microelectronics, etc. [1]. Considerable amount of theoretical studies was published regarding different properties of clusters comprising coinage metals mixed with group 16 atoms [2—4]. Not a long time ago, the structural properties of small clusters $\text{Au}_n\text{S}$, $(n = 1—5)$ and $\text{Au}_n\text{S}_2$, $(n = 1—4)$, and the aspect of gold—sulfur interaction and its effects on the most stable geometries were studied by Bravo-Pérez and Garzón [5]. Recently, our research group studied the coinage metal telluride clusters $(\text{M}_2\text{Te})_n$, $(\text{M} = \text{Cu}, \text{Ag}, \text{Au}; n = 1—3)$ and $\text{M}_n\text{Po}$ $(\text{M} = \text{Cu}, \text{Ag}, \text{Au}; n = 1, 2)$ [6—9]. It was found that the electron correlation effects have a strong influence on the bond angle of the clusters but do not change the bond length significantly. The relativistic effects lead to shorter $\text{M—Te}$ bond length, lower energies, and increased vibrational frequencies. To our knowledge, the structural properties of gold—telluride systems $\text{AuTe}$, $\text{Au}_2\text{Te}$, and $\text{AuTe}_2$, especially the aspect of gold—telluride interaction, electron correlation, and relativistic effects on the structure and stability of clusters have not been studied systematically, neither on experimental nor theoretical basis. However, this type of systems should have a close relationship with the coinage metal—sulfur cluster [5] because of their analogous configuration of valence electrons.

In this paper, the structural properties of gold—telluride systems $\text{AuTe}$, $\text{Au}_2\text{Te}$, and $\text{AuTe}_2$ using quantum-mechanical calculations were investigated. From the calculation, not only an insight was obtained into the energetics of various isomers that have not been measured experimentally, but also the basic information regarding the characteristics of the gold—telluride interaction, electron correlation, and relativistic effects on the most stable geometries of this type of systems. Calculated results are in good agreement with the literature [2—9], thus, we expect that presented data constitute reasonable estimates, even though no experimental data are available at present.

**EXPERIMENTAL**

The Møller—Plesset second-order perturbation
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The electron correlation effects were investigated using the Møller—Plesset second-order perturbation theory method (MP2) and the coupled cluster formalism restricted to single and double excitation augmented by a perturbational estimate for triple excitation (CCSD(T)) theoretical levels employing the relativistic and nonrelativistic energy-consistent pseudopotentials (RECP and NRECP) and basis sets [10]. The relativistic effects on the most stable structures of different isomers were investigated at the MP2 level with the relativistic and nonrelativistic energy-consistent pseudopotentials (RECP and NRECP) and basis sets given by Schwerdtfeger et al. [14, 15].

All calculations were performed using Gaussian98W [16] program package.

RESULTS AND DISCUSSION

The calculated total energy $E$, equilibrium distance $r$, vibrational frequency $\nu$, dissociation energy $D_0$, and total energy of ground state for clusters Te$_2$ and AuTe are reported in Table 1 together with the experimental values. The data calculated for both molecules show good agreement with the experimental values [13, 17], although an improvement of $\nu$ of Te$_2$ might be expected using enlarged basis sets, because the vibrational frequency of Te$_2$ is slightly (58 cm$^{-1}$) overestimated.

The results of calculations indicate that the ground state of neutral Te$_2$ is $3\Sigma_g^-$ dissociating into Te$(2S_g^-)$ + Te$(2S_g^-)$, which is in agreement with the results of Heinemann and Koch [13]. In the case of AuTe, the ground state $2\Sigma^+$ dissociates into Te$(3P_g^+)$ + Au$(2S_g^-)$. According to the data collected in Table 1, the equilibrium bond length and vibrational frequency of AuTe cluster in the ground state is characterized by intermediate values with respect to those of the Au$_2$ [18, 19] and Te$_2$ molecules. On the other hand, the dissociation energy of AuTe molecule shows a weaker bond as compared to the homonuclear molecules, but still reflecting a relatively strong gold—telluride interaction.

Fig. 1 presents all stable isomers obtained by vibrational analysis omitting negative frequencies. Assuming different spin multiplicities, properties of these structures are given in Tables 1 and 2. The results show that the ground state of both clusters, Au$_2$Te and AuTe$_2$, is a bent structure, i.e. isomers $II$ and $IV$ of $C_2v$ symmetry, Au$_2$Te being more stable than AuTe$_2$. The bent structure of both clusters shows relaxed Au—Au and Te—Te distances with respect to the equilibrium distances of Au$_2$ [18, 19] and Te$_2$, but the Au—Te bond length remains essentially unaltered compared to the calculated values for the molecule.

![Fig. 1. The locally stable structures of isomers of coinage metal (M = white ball) tellurides (Te = black ball).](image)

Table 1. Bond Length, Vibrational Frequency, Dissociation Energy, and Total Energy of the Ground State of Te$_2$ and AuTe Calculated at the MP2 Level

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>$r$/Å</th>
<th>$\nu$/cm$^{-1}$</th>
<th>$D_0$/eV</th>
<th>$E$/a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te$_2$</td>
<td>$3\Sigma_g^-$</td>
<td>2.56</td>
<td>191</td>
<td>2.59</td>
<td>-15.777</td>
</tr>
<tr>
<td></td>
<td>$2\Sigma^+$</td>
<td>2.60</td>
<td>150</td>
<td>3.12</td>
<td>-142.50</td>
</tr>
<tr>
<td>AuTe</td>
<td>$2\Sigma^+$</td>
<td>2.63</td>
<td>212</td>
<td>2.42</td>
<td></td>
</tr>
</tbody>
</table>

Taken from Refs. [13] (a) and [17] (b).